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FINAL REPORT ON THE EFFECTS OF ON-SITE SEWAGE DISPOSAL SYSTEMS ON NUTRIENT RELATIONS OF GROUNDWATER AND NEARSHORE WATERS OF THE FLORIDA KEYS

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PROJECT SUMMARY

The effects of on-site sewage disposal systems (OSDS; septic tanks and aerobic treatment units) on nutrient concentrations of upland groundwaters and adjacent inshore waters of the Florida Keys, Monroe County, was studied between December, 1986 and September, 1987. Monitor wells designed to sample groundwater at 8-10 ft below grade were installed at four residential stations in the Upper Keys (Key Largo Limestone substrate) and four residential stations in the Lower Keys (Miami Oolite substrate) to determine the effects of septic tank systems on groundwater quality. A deeper monitor well cluster, consisting of three wells of different depths (15´, 30´, 60´ below grade), was installed adjacent to the injection well of an aerobic treatment unit. Control monitor wells (15´ and 30´ below grade) were located in the pristene environs of the Key Deer National Wildlife Refuge (KDNWR) and remote from potential sources of contamination. All the monitor wells, as well as the most adjacent inshore surface water (i.e. canal), were sampled monthly for determination of ammonium, nitrate, soluble reactive phosphate (SRP), salinity, and temperature.

The results indicated that septic tank/drainfield systems cause extreme nutrient enrichment of groundwaters, which apparently seep into adjacent surface waters through natural groundwater flow patterns. The highest concentrations of nutrients were found in groundwaters adjacent to drainfields and the effluent of the aerobic treatment units, where concentrations as high as 2.5 mM for ammonium, 2.3 mM for nitrate, and 120 µM for SRP occurred. Annual mean concentrations of ammonium and nitrate in residential groundwaters were approximately 350-fold higher than the control, whereas concentrations of SRP were approximately 60-fold higher. The reduced level of SRP enrichment of groundwaters in the Keys appears to be due to mineral formation associated with carbonate geologies (i.e. fluoroapatite) and scavenging by oxides of iron and

aluminum. A significant seasonality was evident for the concentrations of all nutrients in the groundwaters and surface waters; maximum concentrations of groundwater nutrients occurred during winter (minimum during summer), whereas maximum concentrations in surface waters occurred during summer (and minimum in winter). This suggests that maximum discharge of groundwater nutrient loads into surface waters occurrs during summer, which may be due to increased groundwater recharge, hydraulic head (and groundwater flow), and mixing processes during the higher sea levels that occur in summer compared to winter. Approximately three-fold higher concentrations of chlorophyll also occurred in inshore surface waters during summer, apparently in respone to groundwater nutrient enrichment.

Direct determinations of groundwater flow rate at several locations on Big Pine Key during summer 1987 indicated an average flow rate of 2.8 ft/day. However, increased flow was observed in response to ebbing tides (up to 5 ft/day) and rain events (up to 12 ft/day). Direction of groundwater flow could not be predicted as based solely on the decreasing grade elevations to the most adjacent surface water, and explains previous failures of rhodamine dye to trace septic effluents into adjacent surface waters. Based on an average travel path to the down stream receiving waters of 350′ for one canal residence on Big Pine Key, an average of 6 months would be required for discharge of nutrients into surface waters. Considering the expanded tourist and resident population of the Keys during winter, the resulting nutrient load might be expected to reach surface waters during the following summer. Such a "delayed discharge" would be facilitated by increased sea level, groundwater recharge, hydraulic head, and groundwater flow during late spring and summer.

INTRODUCTION

The marine environment of the Florida Keys is one of the most important assets to the economy of Monroe County. The clear, oligotrophic waters of the Keys support extensive growth of corals and seagrasses that are linked directly or indirectly, to tourism, commercial and sport fisheries, and the distinctive "Keys" way of life. To determine potential impacts on the marine environment by increasing use of on-site sewage disposal systems (OSDS), a one year study was conducted to quantify effects of OSDS on nutrient concentrations of upland groundwaters and adjacent inshore waters. Twenty groundwater monitor wells were installed and, together with adjacent inshore waters, sampled for nutrient concentrations (ammonium, nitrate, soluble reactive phosphate) as well as salinity and temperature. Rate and direction of groundwater flow was determined at several sites on Big Pine Key to determine subsurface flow patterns and quantify potential dispersion of septic leachate associated with OSDS in Miami Oolite limestone substrate. Concentrations of nutrients and chlorophyll-a were also measured at hydrographic stations in inshore and nearshore waters along a transect extending from canal waters on Big Pine Key to offshore waters at Looe Key National Marine Sanctuary.

BACKGROUND

The Florida Keys are truly unique in North America in having the most biologically diverse and productive shallow water (<10m) tropical marine ecosystem. The archipelago island chain of the Keys separates the marine environments of Florida Bay and the Gulf of Mexico from that of the Florida Straits and Atlantic Ocean, with numerous tidal passes between the Keys providing water exchange between these water bodies. The most unique feature of the Keys marine environment is the extensive coral reef formations that extend for 220 miles between Soldier Key and Dry Tortugas that include patch and bank reef systems ranging from 25m to 13 km offshore and collectively referred to as the Florida Reef Tract (Vaughn, 1914; Jaap, 1984). Coral reef ecosytems are the most biologically diverse and productive ecosystems on earth (Goreau, 1979) and make tourism and recreation a major factor in the local and regional economy. Several species of tropical seagrasses also form extensive meadows in the shallow Keys marine environment and are important as sources of food and habitat for marine organisms, stabalization of sediments, and recycling and storage of nutrients (Zieman, 1982).

The importance of maintaining water quality with increasing upland development was a major element that spurred legislation to protect the unique Keys marine environment. In 1974, the Florida Keys were designated as an "Area of Critical State Concern" under Chapter 380 of the Florida Statutes. Section 380.0552, "The Principles for Guiding Development in the Florida Keys Area of Critical State Concern" was adopted by the administrative Commission ten years later, in 1984, to "insure a water management system that will reverse the deterioration of water quality and provide optimum utilization of our limited aquatic resources, facilitate orderly and well planned development, and protect the health, welfare, safety, and quality of life of the residents of this state." Subsequently, in 1985, the waters of the Florida Keys were designted as "Outstanding Florida Waters" under Chapter 403 of the Florida Statutes.

In accordance with the guidelines of Section 380.0552 cited above, the use of OSDS for wastewater management in the Florida Keys remains controversial. The bulk (70%) of liquid domestic waste disposal in Monroe County is met by OSDS, either septic tank/drainfield systems or aerobic treatment units, such as the "Multi-Flo" unit, coupled with injection wells. Considering that only 20% of the 53,000 platted, subdivided lots in the Florida Keys are developed at present, cumulative effects of increasing use of OSDS could have potentialy dramatic effects on inshore water quality. While studies of septic tank systems in Dade County, FL have concluded that septic leachate enters surface waters in canals and causes water quality degradation (Barada, 1972) there still exists no general agreement regarding the effects of OSDS on water quality in the Florida Keys.

This lack of general agreement regarding impacts of canalization and septic tank use on water quality in the Keys results from the disparate conclusions of previous studies that have addressed this issue. For example, the studies of Chesher (1973) reported satisfactory water quality in virtually all of the canals studied and concluded that "there were no adverse environmental conditions attributable to septic tanks." However, the studies of Hicks et al. (1974) concluded that canal systems in the Keys have poor flushing characteristics that result in frequent violations of both State and Federal water quality criteria. Furthermore, although dye studies failed to demonstrate septic leachate directly entering canal waters, elevated dissolved nutrients and total organic carbon in developed canals appeared to be responsible for lower oxygen levels in developed compared to undeveloped canals (Hicks et al., 1974).

An assessment of the use of OSDS on inshore water quality of the Keys will necessarily have to address groundwater quality also. Groundwaters are known to be important nutrient sources to lakes (Keeney et al., 1971; Brock et al., 1982; Loeb and Goldman, 1979) but only recently have they been demonstrated as significant nutrient sources to inshore marine waters. For example, groundwaters are an important nutrient source in salt marsh systems on Cape Cod, Massachusetts (Valiela et al., 1978), in nearshore waters of Long Island Sound, New York (Capone and Bautista, 1985), and in back-reef habitats on coral reefs along the north shore of Jamaica (D'Elia et al., 1981). While a historical importance of groundwater nutrient inputs on nutrient budgets of coastal waters is recognized (e.g. Manheim, 1967) increasing development and agriculture in upland, coastal areas are dramatically increasing the role of groundwaters in nutrient budgets of nearshore marine waters (Capone and Bautista, 1985; Pye and Patrick, 1983). The potential for nutrient enrichment of nearshore waters by groundwaters enriched with septic leachate is exacerbated in the Florida Keys because of the high porosity and permeability of its coral-derived substrate and the ubiquitous close proximity of OSDS to oligotrophic marine ecosystems; there also exists the possibility that elevated tides and cross island heads accelerate flow of enriched groundwaters toward oligotrophic marine habitats. Studies of groundwater flow along Florida's east coast have clearly demonstrated brackish groundwater fluxes into nearshore marine waters on the order of 45 m^3/day from a strip one meter wide (Kohout, 1966), suggesting that enriched groundwaters could become a major source of nutrients to nearshore environments in South Florida.

Special concern regarding increased nutrient availability on the ecology of nearshore waters of the Florida Keys is based on the known high degree of nutrient limitation that is key to maintaining outstanding water quality in these oligotrophic waters. Nutrient-limitation bioassays with several species of dominant macroalgae in Pine Channel and Florida Bay demonstrated severe limitation of productivity by phosphorus and nitrogen (Lapointe, 1987; Lapointe, 1988), supporting the the contention that limited nutrient availability regulates, to a large extent, marine plant growth in these waters. Consequently, increased nitrogen and phosphorus flux to nearshore waters of the Keys marine environment could lead to increased marine biomass (phytoplankton and macrophytes) resulting in increased microbial decomposition, decreased submarine irradiance, and cumulative water quality degradation. This process of water quality degradation, referred to as cultural eutrophication, is receiving increased attention by marine scientists who are in general agreement that the process is regulated primarily by nutrient loading (e.g. Ryther and Dunstan, 1971; Lee and Jones, 1981). Cumulative effects of eutrophication include reduced water transparency, reduced dissolved oxygen concentrations, odors (hydrogen sulfide), fish kills, and a reduction of biological diversity. Because inorganic forms of dissolved nitrogen (nitrate and ammonium) and phosphorus (soluble reactive phosphate, SRP) are the most important forms associated with domestic wastewater that support algal growth (Parsons et al., 1977), a knowledge of the contribution of OSDS to concentrations of these nutrients in groundwaters and surface waters of the Florida Keys is needed.

SCOPE OF THE PRESENT STUDY

The objectives of the present study were to:

1) determine if use of OSDS affects nutrient concentrations of upland groundwaters and/or adjacent inshore waters.

2) determine groundwater flow rates in typical geologies of the Keys to quantify interaction of groundwaters with inshore marine waters.

3) Determine the relationship, if one exists, between dissolved inorganic nutrients and phytoplankton chlorophyll in nearshore waters to predict potential effects of increased nutrient availability.

MATERIALS AND METHODS

Study Area

This study took place in Monroe County, FL, and included a variety of residential canal locations that extended from Key Largo in the Upper Keys to Big Pine Key in the Lower Keys. The surafce geology of the Upper Keys is composed primarily of coral reef rock known as Key Largo Limestone whereas that of the Lower Keys is formed of small spherical grains of calcium carbonate cemented together and known as Miami Oolite (Hoffmeister, 1974; Multer, 1971). Key Largo Limestone is very porous and riddled with numerous solution features and voids that allow rapid vertical and horizontal groundwater flow; consequently, this formations retains little fresh water because of its high permeability and therefore, no freshwater lenses occur in the Upper Keys (Parker et al., 1955; Hoffmeister and Multer, 1968). Although Miami Oolite in the Lower Keys is also quite porous, it has fewer horizontal voids than the Key Largo Limestone so retention of fresh water is enhanced and results in several fresh water Ghyben-Herzberg lenses, most notably those of Big Pine Key (Hanson, 1980).

Monitor Wells: Design and Installation

To determine potential effects of septic tank leachate on groundwater nutrient concentrations, nutrient concentrations were determined in groundwaters of 16 monitor wells on eight upland residential lots with septic tank/drainfield systems currently in use and compared to values for pristene groundwaters of the Key Deer National Wildlife Refuge (KDNWR) that were considered the "control"(see list of stations in Table 1 and location of the stations in Figs 1-4). Four stations were selected in the Upper Keys and four in the Lower Keys to address the different geologies of these areas and its possible effects on nutrient relations of groundwaters and inshore waters.

Two monitor wells were installed on each of the eight residential lots. One well was installed in the vicinity of the septic tank drainfield and the other well was installed on the waterfront side of the lot, approximately halfway towards the surface water closest to the septic drainfield. A portable hand-held 1" auger was used to bore a 10′ deep borehole; initial development utilized a portable well point sampler designed for groundwater plume tracking (Kerfoot, 1984). Following development, the boreholes were cased with 1/2 inch PVC pipe that had a 2′ long section of continuous slotted well screen (0.010 of an inch slot width) adjusted to a horizon 8-10 ft below grade at each location. Saturated groundwaters were commonly reached at 3-4 ft below grade at most locations, but we believed that by sampling somewhat deeper groundwaters a more representative and consistent sample of groundwaters would be realized.

To determine potential effects of injection well wastewater on groundwater nutrient concentrations both at depth and in near-surface groundwaters, a site in the lower Keys (Halcyon Trailer Park; See Table 1) with a "Multi-flow" aerobic treatment unit coupled to a 60′ injection well was monitored. At this site, a cluster of three monitor wells, each sampling a different and discrete depth, was installed according to guidelines outlined in Driscoll (1986). From grade, three boreholes (60′, 30′, and 15′) were augered along a transect towards the closest adjacent surface waters from the injection well. These monitor wells were cased with 2" PVC pipe (to also allow groundwater flow determinations, see below) and each casing had a 5′ section of .010 inch continuous slotted well screen at the bottom; annular space in these wells was packed with with coarse carbonate substrate.

These monitor wells meet or exceed published guidelines for monitor well installation for monitoring of dissolved inorganic nutrients as outlined by Driscoll (1986) and for groundwater flow determinations as suggested by Kerfoot (1986); well logs that contain details of the wells (e.g. grade and exact locations of wells) are available from the Monroe County Planning Department.

Sampling of Groundwaters

The monitor wells were sampled monthly following installation, which began in December 1986 and ended in September 1987. Initial groundwater samples were collected with a portable well point sampler (Kerfoot, 1984); after casing of the wells, either a submersible pump fitted with Tygon plastic tubing (for 2" I.D. monitor wells) or a peristaltic pump fitted with teflon tubing was used for sample extraction. Sampling protocal consisted of initially removing approximately 3-5 casing volumes prior to sample collection (Driscoll, 1986). All wellpoint sampler parts, pump tubing and fittings were rinsed with tap water between well samplings to prevent cross contamination of different groundwater samples.

Collection and preservation of the groundwater samples followed the methodologies suggested in Standard Methods (Greenbaum, 1975). Specifically, protocal consisted of sample collection into acid-washed 1 liter Nalgene polyethylene containers, immediate determination of temperature (using a mercury thermometer) and salinity (using a Bausch and Lomb hand-held refractometer) and subsequent preservation with a biocide (10mg/l HgCl). The samples were held on ice in the dark until return to the laboratory where they were immediately filtered through a 0.45 μ Gelman glass fiber filter and either analyzed immediately for nutrient analysis or frozen for subsequent analysis (within 2 weeks).

Determination of Groundwater Flow Rate and Direction

To understand interactions of groundwaters with inshore surface waters, a knowledge of the direction and rate of horizontal subsurface flow is needed. Direct determinations of the rate and direction of groundwater flow were made at several locations on Big Pine Key using a Model 30 GeoFlo groundwater flowmeter (K-V Associates, Inc; Falmouth, MA). This flowmeter is a portable, self-contained system that allows direct measurement of the rate and direction of lateral flow of groundwater through permeable saturated geologies. The Model 30 GeoFlo flowmeter uses a submersible sensor consisting of a circular array of thermistors arranged around a central heat source. A five vector response is displayed on an LCD readout which, in combination with a calibration curve and vector worksheet, can allow determination of groundwater flow rate in the range of .03-500 ft/day (+ 15%) and direction of groundwater flow (+ 10%).

The accuracy and precision of the GeoFlo flowmeter is greatly affected by monitor well design and calibration of the flowmeter; therefore, procedures suggested by the manufacturer were closely followed (See Kerfoot, 1986). The GeoFlo flowmeter was deployed in 2" I.D. PVC monitor wells that had sections of slotted well screen inserted at desired depths below grade. This involved use of a high quality, continuous slotted well screen (Timco, sch 40, .010 inch slit width, 59 slots per foot), centralization of the well, and careful annular packing with washed, coarse carbonate substrate. Groundwater flow monitor wells were installed at several locations on Big Pine Key and include three wells at Halcyon Trailer Park (HTP, see above description of monitor well installation) as well as two wells (15′ and 30′) in the Key Deer National Wildlife Refuge (KDNWR) and one well (15′) in Port Pine Heights subdivision (PPH, See Table 1).

Calibration of the GeoFlo flowmeter involved use of a flow chamber packed with carbonate substrate similar to that surrounding the monitor wells (Miami Oolite) and a metering pump to provide controlled and variable flow rates. A typical calibration curve for the GeoFlo flowmeter in Miami Oolite substrate is illustrated in Fig 5; regression of the readout of the GeoFlo versus known rates of lateral flow allows rapid, on-site determination of groundwater flow rates. The five vector response is used with a worksheet to test for uniform cosine flow and then plotted on polar graph paper to determine direction of flow. Field logs for all groundwater flow determinations are available from Monroe County Planning Department.

Sampling of Surface Waters

During the monthly sampling at the eight residential monitor stations and the "Multi-Flo" station on Big Pine Key, samples of adjacent surface waters were also collected for determination of nutrient concentrations. Samples were collected either by hand using a 3 liter Nalgene container or using a 3.7 liter Niskin bottle sampler. Surface water samples were also collected at monthly intervals along an onshore-offshore transect extending from an inshore canal system (PPH) on Big Pine Key to Looe Key National Marine Sanctuary (LKNMS), located 5 miles south of Big Pine Key; the hydrographic stations along this transect are listed in Table 2 and locations are illustrated in Fig 6. Surface water samples collected from canals adjacent to the residential stations were handled in identical fashion to that described above for groundwater samples; however, the transect samples, which were also analyzed for chlorophyll-a, were not spiked with a biocide because of interference with the chlorophyll analysis.

Nutrient and Chlorophyll Analysis: Methodologies and Quality Assurance

Surface and groundwater samples were analyzed for dissolved inorganic nitrogen in the form of nitrate, nitrite and ammonium using a Technicon Autoanalyzer II system. Preliminary analyses indicated that nitrite was negligible compared to nitrate in groundwater and surface water samples at all stations; comparable results have also been reported for similar carbonate groundwaters and inshore waters of Bermuda (Simmons et al., 1984) and Jamaica (D'Elia et al., 1979). Therefore, we determined and report herein total nitrate and nitrite (referred to as nitrate, NO_3) using the copper-cadmium reduction method according to standard Technicon Industrial methodology (Technicon,1972). The ammonium determinations were made using a modified phenol-hypochlorite method described by Slawyk and MacIssac (1972). Nutrient concentrations are reported in units of μM (= μg-at/l) to conform with the marine chemistry literature. The detection limit during these analyses was 0.10 μM for nitrate and 0.20 μM for ammonium.

Because phosphate appears to be the primary limiting nutrient in the nearshore Keys marine environment (Lapointe, 1987; Lapointe, 1988) and is present at very low concentrations (e.g. frequently < 30-50 nM), concentrations of soluble reactive phosphate (SRP) were determined using the highly sensitive manual method described by Strickland and Parsons (1977). This method is a modification of the Murphey and Riley (1962) molybdenum blue method and utilized a Bausch and Lomb spectrophotometer 88 fitted with a 10 cm. cell for maximum sensitivity.

Quality assurance of our nutrient determinations is based on known internal standards that were analyzed regularly with all unknown samples. A continuous record of analyses of standards and recoveries was maintained and assures that our determinations were accurate and within acceptable upper and lower limits (EPA, 1972). Interlaboratory comparisons of unknown samples (available from EPA) indicated that mean recoveries for our nutrient determinations are excellent and range from 95-103% of stated EPA values.

Chlorophyll-a concentrations of seawater were determined using a Turner Designs Model 10 fluorometer that was calibrated using known concentrations of chlorophyll. A 800 ml seawater sample was filtered through a 0.45 μ Gelman glass fiber filter and analyzed for chlorophyll-a using a modified dimethyl sulfoxide (DMSO)-acetone method (Burnison, 1979). Immediately following filtration, the filters were placed in 10 mls DMSO in a cool, dark place to extract for one hour; following this, 15 mls of acetone was added. After two hours of further extraction, the samples were analyzed for fluorescence. Subsequent acidification with 10% HCL was also performed to correct for phaeophytin.

Statistical Analyses

Several hypotheses were tested in this study. First, to consider potential effects of OSDS on nutrient concentrations (ammonium, nitrate, and SRP) of groundwaters in the Florida Keys, groundwater nutrient concentrations of the eight residential monitor stations were compared to nutrient concentrations of the "control" station at the KDNWR. Specifically, the following null and alternative hypotheses were tested:

H_o: nutrient concentrations of groundwaters adjacent to OSDS are equal to those of groundwaters of the KDNWR.

H_A: nutrient concentrations of groundwaters adjacent to OSDS systems are greater than groundwaters of the KDNWR.

Second, to consider potential seasonal seepage of nutrients from groundwaters into the nearshore marine environment due to climatological forcing, nutrient concentrations (ammonium, nitrate, SRP) of groundwaters and nearshore marine waters (canal waters adjacent to sites) at the eight residential OSDS sites during winter (December-April) were compared to those of summer (May-September). Specifically, the following null and alternative hypotheses were tested:

H_O: nutrient concentrations of groundwaters during winter are equal to those of summer.

H_A: nutrient concentrations of groundwaters during summer are lower than those of winter.

H_O: nutrient concentrations of inshore marine waters are the same in summer and winter

H_A: nutrient concentrations of inshore marine waters are higher in summer than winter.

These a priori hypotheses were tested using the Kruskall-Wallis test, a conservative nonparametric test statistic. The experimental design involved comparisons of data within individual stations to reduce station-to-station variability and increase the power of these statistical tests. Because of the sensitivity of our nutrient analyses and the randomized block experimental design, we used a conservative alpha level of P=0.05 to represent the probability of making a Type I error; thus, significance reported in the results below indicates the probability of making an incorrect inference is <0.05 or less than 1 chance in 20.

RESULTS

Groundwater Nutrient Concentrations

Concentrations of ammonium, nitrate, and SRP as well as salinity and temperature of groundwaters sampled at monthly intervals between December 1986 and September 1987 from groundwater monitor wells at the eight septic sites and KDNWR are presented in Appendix Table 1. The highest groundwater nutrient concentrations generally occurred during winter at the septic locations; lower concentrations occurred at the midpoint locations and the lowest concentrations typically occurred in groundwaters of the KDNWR. Over the entire study, ammonium and nitrate concentrations ranged from 0.77 μM to 2.75 mM and 0.03 μM to 2.89 mM, respectively; SRP concentrations ranged from 0.06 μM to 107.4 μM (Table 3). Salinity of the groundwater samples ranged from 0% (fresh) to 27% (saline) and temperature ranged from a low of 21.0°C in January to a high of 32.0°C in August (Table 3).

Nutrient concentrations in groundwaters did not vary significantly between the Upper and Lower Keys, but an overall seasonal trend was evident. Concentrations of ammonium, nitrate, and SRP in groundwaters from a majority of the monitor wells decreased significantly from winter to summer, 1987 (See Table 3). Overall, nutrient concentrations decreased from winter to summer in 8 out of 13 monitor wells for nitrate (Table 4), 7 out of 13 wells for ammonium (Table 5), and 8 out of 13 wells for SRP (Table 6). The average groundwater nutrient concentration (average of both septic and midpoint locations) during winter was 541 μM for ammonium, 494 μM for nitrate, and 10.3 μM for SRP; the average concentration during summer was 345 μM for ammonium, 125 μM for nitrate, and 4.0 μM for SRP (Table 3).

Nutrient concentrations of groundwaters at the KDNWR "control" station did not vary significantly from winter to summer and were consistently lower than nutrient concentrations characteristic of the residential stations. During winter, nutrient concentrations averaged 1.91 μM for ammonium, 0.76 μM for nitrate, and 0.11 μM for SRP; during summer, nutrient concentrations averaged 1.40 μM for ammonium, 0.20 μM for nitrate, and 0.14 μM for SRP (Tables 4-6).

A comparison of groundwater nutrient concentrations from the residential stations and the KDNWR station indicates significantly elevated nutrient concentrations on developed, residential lots with septic tank/drainfield systems. For example, concentrations of ammonium, nitrate, and SRP during winter were all significantly higher in residential groundwaters compared to groundwaters in the KDNWR in all 24 cases analysed; during summer, 17 out of 24 cases indicated significantly elevated nutrient concentrations in residential groundwaters compared to groundwaters of the KDNWR (Table 7). The various nutrients were enriched in residential groundwaters, relative to groundwaters of the KDNWR, some 625 to 650-fold for nitrate, 246 to 283-fold for ammonium, and 29 to 94-fold for SRP.

Nutrient concentrations of groundwaters adjacent to the "Multi-Flo" injection well were also significantly elevated compared to those of the KDNWR. During summer, concentrations of ammonium and SRP averaged 19.1 μM and 0.67 μM, respectively, about 5-fold higher than concentrations of 3.35 μM and 0.12 μM for ammonium and SRP, respectively (Table 8). Concentrations of ammonium and SRP were approximately the same at different depths at the "Multi-Flo" site (15′ to 60′) whereas ammonium concentrations appeared to increase with depth at the

KDNWR. Salinity increased with depth at both sites and waters at 60´ at the "Multi-Flo" site were always hypersaline (Table 8).

Groundwater Flow

Direct measurement of groundwater flow indicates that rainfall and tides affect the instantaneous lateral velocity of subsurface groundwater movements. At Port Pine Heights (PPH) on Big Pine Key, groundwater flow rate ranged between 0 and 5.0 ft/day during an ebbing tide on July 24 1987 with the lowest rates occuring during peak high tide and highest rates occuring during the ebbing tide (Fig 7); over the full 12 hrs of the ebbing tide, the flow rate averaged 2.3 ft/day (Table 10). On October 2 1987, groundwater flow rate at the same site during a flooding tide ranged between 2.8 and 12.1 ft/day with anomoulously high flow rates occurring between 2130 and 2300 hrs when a major rain event occurred (>1.0 inches of rain fell in 6 hrs; Fig 8); the average flow rate during this flooding tide was 5.5 ft/day (Table 9). During both groundwater flow studies, the direction of groundwater flow ranged between 163° and 222° and averaged 184° or southward (Table 9).

Groundwater flow rates in the KDNWR monitor wells (15´ and 30´ wells) ranged from 0 to 4.10 ft/day and averaged 2.1 ft/day; the direction of flow at both depths was consistently between 71° and 104°, or eastward (Table 10). However, flow rates were greater in the deeper (30´) Key Largo Limestone formation, which averaged 3.7 ft/day and ranged from 3.38 to 4.10 ft/day; flow rates in the shallower Miami Oolite (15´) averaged 0.38 ft/day and ranged from 0.0 to 0.75 ft/day.

Groundwater flow rates at the Halcyon Trailer Park monitor wells (15´, 30´, and 60´) averaged 2.2 ft/day and ranged from 2.17 to 3.38 ft/day; no differences in flow rate at different depths were apparent. However, at this station, direction of groundwater flow was different between the different depths; flow at 15´ was 197° or southwestward whereas flow at 60´ was 305° or northwestward (Table 10).

Surface Water Nutrient Concentrations and Chlorophyll

Concentrations of ammonium, nitrate, and SRP as well as salinity and temperature of surface waters sampled at monthly intervals between December 1986 and September 1987 from inshore waters adjacent to the groundwater monitor wells at the eight residential sites and KDNWR are presented in Appendix Table 1. A significant seasonal trend opposite that of groundwaters was observed for the inshore waters; consistently, the lowest nutrient concentrations occurred during winter and the highest occurred during summer (Table 4-6). For example, concentrations of nitrate ranged from 0.27 μM to 4.05 μM during winter and from 0.28 μM to 49.02 μM during summer; ammonium ranged from 0.15 μM to 2.39 μM during winter and from 0.33 μM to 6.92 μM during summer; SRP ranged from 0.03 μM to 0.35 μM during winter and from 0.12 μM to 1.60 μM during summer (Table 3).

In all 12 surface water samplings along the hydrographic transect, nutrient concentrations and chlorophyll consistently decreased towards offshore waters. Over all these samplings, concentrations of nitrate ranged from 0.08 μM (LKNMS) to 3.02 μM (PPH canal), ammonium ranged from 0.02 (LKNMS) to 0.94 μM (PPH canal), SRP ranged from 0.03 μM (LKNMS) to 0.29 μM (PPH canal) and chlorophyll ranged from 0.04 μg/l (LKNMS) to 0.78 μg/l (PPH canal; Table 11; Appendix Table 2). Out of the twelve samplings, chlorophyll was significantly and positively ($r > 0.70$) correlated with SRP six times, with ammonium twice, and with nitrate three times (Table 12).

Chlorophyll concentrations were significantly greater during summer compared to winter in the inshore waters during these studies. Mean chlorophyll concentration in PPH canal waters during winter were 0.22 μg/l (+ 0.08, N = 16), about three-fold lower than the mean value of 0.62 μg/l (+ 0.19, N =10) during summer.

DISCUSSION

OSDS as a Nutrient Source to Groundwaters and Nearshore Waters

Elevated nutrient concentrations in residential groundwaters compared to pristene groundwaters in the Florida Keys indicates that OSDS represent a significant source of nutrients to groundwaters of the Florida Keys. It is unlikely that the high concentrations of ammonium (2.5 mM), nitrate (2.5 mM) and SRP (30 μM) observed in residential groundwaters would result from a natural source such as the decomposition of leguminous matter, nitrogen fixation, or rainwater (D'Elia et al., 1979). That nutrient concentrations were generally higher at the septic locations compared to midpoint locations during the study clearly point to a septic drainfield source for these elevated nutrient concentrations. Furthermore, the highest nutrient concentrations observed in groundwaters during this study are typical of secondarily-treated wastewater, characterized by concentrations of 2-3 mM of inorganic nitrogen (either in the form of ammonia or nitrate, depending on the degree of oxidation of effluent) and 200-300 μM inorganic phosphate (Ryther et al., 1975; Goldman and Ryther, 1975), and are probably represent groundwater septic plumes. These nutrient concentrations are also typical of effluents sampled from several aerobic treatment units ("Multi-Flo") during this study.

Clearly, and not surprisingly, use of OSDS is resulting in increased nutrient concentrations of associated groundwaters. The mean SRP concentration of residential groundwaters (both midpoint and septic locations) was 10.3 μM during winter and 4.0 μM during summer, considerably higher than background SRP concentrations of 0.11 μM to 0.14 μM in the KDNWR during winter and summer, respectively. Thus, SRP concentrations of enriched groundwaters on residential sites of the Keys were on the order of 29- to 94-fold higher than background concentrations with an annual average of 60-fold higher SRP concentrations. For nitrogen, even higher enrichment occurred. The average total nitrogen concentration (IN = ammonium and nitrate) on residential stations during winter was 1036 μM, compared to a lower value of 471 μM during summer. Relative to background concentrations in the KDNWR, this represents a 370 to 346-fold increase during winter and summer, respectively, with an annual average of 358-fold increase above background concentrations.

Elevated N:P molar ratios of enriched residential groundwaters during this study suggests that SRP is, to some extent, scavenged during flow through carbonate geologies. The N:P ratio of groundwaters (both the septic and midpoint locations) ranged from 94:1 to 147:1, much higher than the 10:1 molar ratio typical of domestic wastewater (Ryther and Dunstan, 1971). In carbonate geologies, SRP is well known to react and co-precipitate with calcium carbonate to form calcium carbonate-phosphate surface complexes and/or the mineral apatite (Berner, 1981); additionally, SRP can be scavenged by adsorption onto oxides of iron (II), iron (III), and aluminum (III). In both oxic and anoxic sulfidic sediments, apatite formation is considered the dominant mineral sink of phosphate. The two primary minerals are fluroapatite ($Ca_5(PO_4)_3F$) and hydroxyapatite ($Ca_5(PO_4)_3OH$), with the fluoride-rich form being the most predominant form in marine sediments. Consequently, concentrations of SRP are often low in natuarl carbonate-rich waters because of equilibrium with carbonate fluoroapatite (Gulbrandsen and Robertson, 1973). However, while removal of SRP by calcium carbonate in upland groundwaters appears to be efficient when based on N:P molar ratios, SRP is not completely removed from enriched groundwaters as described above by comparison of residential groundwaters to those of the KDNWR.

Accordingly, upland watersheds of the Keys enriched by OSDS appear to be geochemically phosphorus-limited regarding their stoichiometric impact on nearshore primary production. The most widely used approach to identify the relative importance of nitrogen versus phosphorus limitation is through determination of N:P ratios of seawater and comparison of these ratios with those of marine plant populations. This approach is based on extensive analyses of marine plankton and dissolved inorganic nutrients, both of which indicate an average N:P ratio of 16:1 by atoms in oceanic waters (Redfield, 1958). Deviations of either marine plant composition or seawater nutrients from this ratio is then used as an indirect method to infer which nutrient element limits productivity; N:P ratios $< 10:1$ indicate N-limitation wheras ratios$> 30:1$ indicate P-limitation. While enriched groundwaters are clearly P-limited in that N:P ratios are typically > 94, surface waters in canals during this study had average ratios of ranging from 11 to 17, suggesting a trend towards N limitation in enriched inshore receiving waters. However, frequent correlation of SRP and chlorophyll-a in our nearshore transect studies suggest that elevated SRP is the primary limiting nutrient to phytoplankton production, a conclusion also reported for phytoplankton on the northwest Florida continental shelf (Myers and Iverson, 1981). These results also concur with macrophyte bioassays in nearshore waters of the Keys and Florida Bay where productivity was limited primarily by phosphorous and secondarily by nitrogen (Lapointe, 1987; Lapointe, 1988). A similar predominance of P-limitation occurs in carbonate-rich waters of Shark Bay, Australia, (Smith and Atkinson, 1984) and contasts precepts of nitrogen rather than phosphorus limitation of marine productivity in clastic environments of temperate climes (Ryther and Dunstan, 1971).

Our conclusion that elevated nutrient concentrations of groundwaters in residential areas of the Florida Keys are anthropogenic in origin are in agreement with similar conclusions for Bermuda (Simmons et al., 1984) that were based on elevated concentrations of nitrate in groundwaters and use of cesspits as the dominant form of domestic wastewater disposal. However, while the major form of inorganic nitrogen in Bermuda's groundwaters is nitrate, groundwaters of the Keys have higher concentrations of ammonium compared to nitrate. For example, the mean concentration of nitrate in Bermuda's groundwaters is 749 μM (ammonium is negligible) compared to the Keys where the annual mean concentration of total inorganic nitrogen is 753 μM and consists of 310 μM nitrate and 443 μM of ammonium.

We believe this difference in nitrogenous composition of groundwaters between Bermuda and the Florida Keys is significant and suggests generally low oxygen availability in groundwaters of the Keys. Ammonium represents the most reduced species of inorganic nitrogen and results from decomposition of organic matter in oxygen-depleted waters; in the presence of oxygen, ammonium is rapidly oxidized to nitrite and subsequently to nitrate by nitrifying bacteria. The apparent lack of adequate oxic conditions needed to support oxidation of OSDS wastewater (e.g. ammonium) in shallow groundwaters may be related to the limited vadose zone underlying drainfields associated with OSDS in the Keys; an average of 12" of vadose zone (above mean high water) separates drainfield wastewater from the piezometric (hydrated groundwater) surface in the Keys. Considering that groundwaters typically have low oxygen tensions even without impacts of organic wastes, those impacted by organic wastewater loads will become suboxic or anoxic. Because microbial mineralization of wastewater is much more rapid under aerobic conditions, septic tank/drainfield systems with such limited vadose zones may not provide complete oxidation of their wastewater, as suggested by the elevated ammonium concentrations of residential groundwaters found in this study. As a consequence of impacting low oxygen groundwaters with organic wastewater and associated oxygen demands (both BOD and COD), biogeochemical zones (e.g. sulfide reduction zone that produces hydrogen sulfide) usually restricted to deeper anoxic groundwaters will shift upward towards to near-surface levels, increasing the occurrence of hydrogen sulfide odors to the atmosphere. In contrast to ammonium that was characteristic of septic tank enriched groundwaters, effluents of the aerobic treatment units were composed primarily of nitrate, indicating a better-oxidized effluent.

The significant decrease of groundwater nutrient concentrations and parallel increase in nutrient concentrations of inshore surface waters during summer suggests that nutrients derived from enriched groundwaters are discharged to adjacent inshore waters, to a large extent, in a seasonal manner. This finding contrasts the view that groundwater nutrient concentrations are relatively constant compared to surface waters (Freeze and Cherry, 1979). Considering that all the residential stations used in our study were located on canal sytems, which effectively increase shoreline development and decrease groundwater dilution potential, then mixing and seepage of enriched groundwaters with inshore surface waters is dramatically enhanced. Based on elevated ammonium and total organic carbon concentrations in developed canals compared to undeveloped canals, Hicks et al. (1975) also concluded that septic leachate enters surface waters and be partially responsible for observed ecological imbalances in adjacent waters. Considering the dramatic seasonality in extent of groundwater intrusion to inshore waters, we sought to explain this phenomena by considering the various mechanisms that regulate groundwater seepage to inshore receiving waters.

Mechanisms of Groundwater Seepage to Inshore Waters

In general, nutrients associated with fresh groundwaters enter adjacent surface waters primarily through horizontal groundwater flow, although inclined and vertical flow can also occur (Visher and Mink, 1964; Cooper, 1959; Kohout, 1960). The general direction of flow is offshore because of decreasing hydraulic gradients between the piezometric surface on land and sea level at adjacent inshore surface waters where seepage through canal walls or bottom sediments occurs.. The instantaneous rate of groundwater flow is a function of porosity and permeability of the substrate and hydraulic head. Direct determination of groundwater flow rates in the Lower Keys (PPH) during summer 1987 indicated average instantaneous groundwater flow rates in Miami Oolite substrate of 2.8 ft/day (omitting higher flow rates during rain events), a value consistent with the known high porosity of this geology (bulk porosity of 40-60%; Evans, 1983). Distinctly lower flow rates were associated with Miami Oolite in the KDNWR on Big Pine Key where flow rates ranged from 0 to 0.75 ft/day, a finding consistent with the ability of this geology to support a Ghyben-Herzberg fresh water lens (Hanson, 1980).

Our observed decrease of dissolved nutrients in groundwater and simultaneous increase in adjacent surface waters during summer suggests that a seasonal climatic or astronomical forcing mechanism enhances flow rates of nutrient-rich groundwaters into surface waters. Such a dramatic discharge would require enhanced lateral groundwater flow during summer compared to winter, and would be best explained by increased hydraulic head of groundwater during summer compared to winter. Although freshwater recharge to groundwaters of the Keys is ordinarily maximum during the "wet" summer and early fall in the Keys and could explain seasonal differences in hydraulic head, such a typical rainfall pattern did not occur during this study (NOAA weather, Key West) and no significant seasonal correlation between rainfall and nutrient concentrations of groundwaters and surface waters was apparent.

However, seasonal patterns in tide height did covary significantly with our observed patterns for dissolved nutrients. Sea level is generally acknowledged as the dominant component of fluctuations of groundwater surfaces on carbonate oceanic islands (Hanson, 1980; Rowe, 1984), although rainfall becomes the more important factor during periods of heavy rain (Hanson,1980). Annual variations of 0.8′ in sea level occur in the Keys in response to astronomical, isostatic, and mass transfer effects (Marmer, 1954; Pattullo, 1963) and results in maximum sea levels and groundwater tables during summer and fall at which time the minimum seasonal potential evapotranspiration from groundwaters occurs (the maximum evapotranspiration occurs during the "dry" winter months). Consequently, a seasonal maximum in hydraulic head could occur during summer and fall, during which the mixing rate of fresh groundwaters and marine surface waters would result due to increased inclined flow (Visher and Mink, 1964) and subsurface dispersion (Cooper, 1959; Kohout, 1960). This possibility is directly supported by monthly average sea level and groundwater table height data reported by Hanson (1980) for Big Pine Key and illustrated in Fig 9; the increased hydraulic head during summer and early fall would support increased lateral flow compared to reduced hydraulic head and flow during winter and early spring. Such a seasonal mechanism is also supported by the elevated salinities commonly observed in groundwaters of the Keys during summer as compared to winter (Table 3).

While groundwater flow rates may vary seasonally as a function of hydraulic head and regulate seasonal patterns in discharge of nutrients to inshore waters, the most dramatic increases in groundwater flow occurs on shorter time scales (i.e. hours-days) during rain events. Lateral groundwater velocities up to 12 ft/day occurred during rain events, causing rapid increases in groundwater discharge to inshore waters that were some 5- to 7- fold higher than background flow rates. The rapid flow response and lack of long lag periods of increased flow is consistent with the high porosity and permeability of carbonate geologies of the Keys. This finding also explains the algal blooms that often follow major rain events in inshore waters of the Keys (personal communication).

The direction of lateral, shallow groundwater flow appears to be related primarily to the direction of the hydraulic gradient as affected by large scale natural elevation grades and not necessarily by smaller scale man made changes. For example, groundwater flow at the PPH residential station on Big Pine Key was consistently (14 determinations over 3 months) southerly, the direction of decreases in natural grade, even though the most adjacent surface water body (canal) was 50′ to the west of the flow monitor well. Previous studies using Rhodamine dye injections into septic tanks on Big Pine Key failed to detect septic leachate entering adjacent canal waters (Hicks et al., 1975), quite possibly because the surface waters sampled for dye intrusion were not downstream of the groundwater flow from the septic tank drainfield. Future dye studies in the Keys need to obtain preliminary information regarding natural subsurface flow patterns to support the assumptions generally made in such tracer dye studies.

Patterns and Effects of Nutrient Flux to Nearshore Waters of the Keys

By assuming an average groundwater flow rate and path length to probable receiving waters (not necessarily the closest surface water), the travel time of nutrients associated with groundwaters towards surface waters can be estimated. For example, assuming an average flow rate of 2.0 ft/day for nutrients associated with groundwaters and an average travel path of 350′ to inshore waters typical of the OSDS in our study, a travel time of approximately 0.5 yrs would be required for discharge of new septic-derived nutrients into surface waters. This suggests that seasonally increased nutrient input during the winter tourist season would require about 6 months before discharge to inshore waters, resulting in "delayed discharge" that would exacerbate increased flow of groundwaters into surface waters during summer months. Considering that irradiance and temperature are also maximum during summer, ideal conditions favoring phytoplankton blooms result. A similar delayed discharge of nutrients occurs on Cape Cod, MA, where nutrients introduced to groundwaters during the summer tourist season are discharged to surface waters during winter (Kerfoot, personal communication).

The effects of increased nutrient seepage to nearshore waters of the Keys will be cumulative enhancement of natural eutrophication processes that will result in further water quality degradation. Because the productivity and nutrient dynamics of inshore waters of the Keys are controlled to a large extent by benthic macrophytes that are themselves nutrient limited (Lapointe, 1987; Lapointe, 1988), increases in biomass of marine macrophytes, both seagrasses and macroalgae, will undoubtedly occurr. Quite possibly, previous nutrient enrichment has enhanced historic seagrass and macroalgal growth rates, resulting in the extensive seagrass biomass harvests that are increasingly affecting canals and shorelines when their harvested biomass decomposes, causing local reduction of dissolved oxygen and strong hydrogen sulfide odors.

Several examples serve to illustrate the initially subtle but often devastating ecological imbalances that cultural eutrophication can have on benthic marine ecosystems. Reef corals in Kaneohe Bay, Hawaii slowly became overgrown with the green "bubble alga" _Dictyospheria_ that bloomed in response to nutrient enrichment from a secondary sewage outfall; diversion of the sewage outfall to an offshore location has since partially restored water quality (Smith, 1981). In inshore waters of Bermuda, the green alga Cladophora prolifera has increased dramatically over the past ten years in response to nutrient enrichment by groundwater seepage resulting from widespread use of unlined cesspits (Lapointe and O'Connell, 1988); this has resulted in water quality degradation of Harrington Sound, including loss of the commercially-valuable Calico clam, as well as cave systems that border Harrington Sound - some of Bermuda's major tourist attractions (Ileffe et al., 1984). Phytoplankton blooms resulting from sewage enrichment of Hillsborough Bay, FL (adjacent to Tampa) caused reduction of seagrass biomass and replacement by the red alga Gracilaria (Taylor et al., 1973), a phenomenon that has also occurred in many other inshore areas of Florida.

However, effects of eutrophication will not be limited solely to enhanced growth of marine macrophytes. The significant correlation of phytoplankton chlorophyll and dissolved nutrients, particularly SRP, during our study suggests that cumulative nutrient enrichment of inshore waters of the Keys will also result in a trend toward increased phytoplankton biomass that could cause the most dramatic water quality degradation. Increased phytoplankton chlorophyll concentrations are well known to degrade seagrass and coral reef ecosystems by decreasing water transparency, submarine irradiance, dissolved oxygen, biotic diversity and secondary production (e.g. see Zieman, 1982; Johannes, 1975). Furthermore, blooms of the toxic red tide dinoflagellate species are increasing world-wide in waters adjacent to developing coastlines, sugessting that run-off derived from mans activities favor initiation of these devastating blooms. Red tides of Gymnodinium breve on the east coast of Florida in 1972 originated from seed that was carried from the west coast of Florida through the Keys to the

CONCLUSIONS and RECOMMENDATIONS

1) Based on the demonstrated extreme nutrient (ammonium, nitrate, and SRP) enrichment of residential upland groundwaters by OSDS as well as observed discharge of these nutrients into inshore waters, most notably during summer and early fall and during rain events, we concur with conclusions of Hicks et al. (1975) that water quality of inshore waters of the Keys is measurably impacted by use of OSDS. As described by Hicks et al (1975), such impacts result in frequent and gross violations of established Class III water quality criteria regarding dissolved oxygen and biological integrity. Our results are also in agreement with those of Pitt et al (1975) that also reported septic leaching into groundwaters and found that hydraulic conductivity was the primary factor controlling the extent of groundwater contamination. We further suggest that increased growth of marine plants, both phytoplankton and macrophytes, results from this enrichment and that this biomass production exacerbates background BOD arriving in inshore waters with nutrient enriched groundwaters. Our results do not support the conclusion of Chesher (1974) that " there are no adverse environmental conditions (in canal waters) attributable to septic tanks "; in assessing that study, we believe that inadequate methodology and bias confounded interpretation of data and precluded valid inferences.

2) Cumulative impacts of nutrients associated with OSDS as well as ancillary but related sources, should be quantitatively assessed on an areal basis prior to permitting of development of upland recharge areas of any inshore or nearshore waters that are to be given the highest degree of environmental protection. The following standards, adapted

from the Planning Board of the Town of Falmouth, MA, are given as an example:

a) Loading per person: 5 lbs nitrogen/person/year; .25lbs phosphorus/person/year for OSDS within 300 ft of shoreline. Persons per dwelling unit = 3.0

b) Loading from lawn fertilizers: 3 lbs nitrogen/1000 ft^2/year

c) Loading from road runoff: .19 lbs nitrogen/curb mile/day; .15 lbs phosphorus /curb mile/day

d) Critical marine eutrophic levels: 16 lbs N/40,000ft^2/yr

While the above loading rates represent a long-term national average, the critical eutrophic levels cited above are specific to Cape Cod waters (i.e. nitrogen-limited marine waters compared to phosphorus limited waters in the Keys). We suggest that a study be performed to provide a quantitative data base (i.e. flushing rates, concentrations of inorganic and organic nutrients, dissolved oxygen, chlorophyll, etc.) that would allow development of accurate critical eutrophic levels specific to inshore marine waters of the Keys.

3) Increased use of waste treatment should be considered for high density, platted subdivisions that clearly are in excess of critical eutrophic levels as cited above. A study should also be conducted to consider cost/benefit relationships of various types of waste treatment suitable for the Keys, which needs to include assessment of improved OSDS (i.e. better drainfield designs), alternate sewers (Godfrey, 1986) coupled to aerobic and/or tertiery treatment facilities (assessing potential use of mangrove systems to strip nutrients), ocean outfalls (Officer and Ryther, 1977), and deep (below an aquiclude) well injection. In advanced waste treatment

designs, priority should be placed on phosphorus stripping as this nutrient appears to limit eutrophication and, compared to nitrogen, is more easily removed from wastewater effluents.

4) Considering the unique marine resources of the Florida Keys and the importance of maintaining adequate water quality to the economic well-being of Monroe County, a water quality monitoring program specifically designed to address nutrient enrichment via groundwater seepage, wastewater outfalls, and stormwater runoff and related eutrophication of adjacent surface waters needs to be initiated. A majority of experts in the water quality field believe that eutrophication is potentially the most severe source of degradation of natural waters (Clark et al., 1977). Such a monitoring program should address the current status of water quality in Monroe County and also use whatever existing historical data bases are available to document any significant degradation. In addition to nutrients, groundwaters are often contaminated by a spectrum of synthetic organic and metal pollutants. Thus, the identification in the present study of nutrient enrichment from groundwaters suggests that this is an additional route that should be monitored for transfer of persistent metal and organic pollutants to inshore waters of the Keys.

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TABLE 1. Key to abbreviations for groundwater monitoring stations.

ABBREVIATION	STATION
KDNWR	Key Deer National Wildlife Refuge
PPH	Port Pine Heights, Big Pine Key, FL
EP	Eden Pines, Big Pine Key, FL
DA	Doctor's Arm, Big Pine Key, FL
WP	Whispering Pines, Big Pine Key, FL
DL	Dodge Lake, Marathon, FL
YT	Yellow Tail, Marathon, FL
TH	Treasure Harbor, Plantation Key, FL
OS	Ocean Shores, Key Largo, FL

TABLE 2. Hydrographic monitoring stations and locations in nearshore waters of Big Pine Key, FL.

STATION	LOCATION	LAT/LON
1	Port Pine Heights finger canal	24°42.88´N 81°23.87´W
2	Port Pine Heights main canal	24°42.86´N 81°23.88´W
3	South Pine Channel	24°41.58´N 81°24.50´W
4	Munson Island	24°38.30´N 81°23.64´W
5	Hawks Channel	24°34.13´N 81°23.62´W
6	Looe Key National Marine Sanctuary Back Reef	24°32.90´N 81°23.46´W
7	Looe Key National Marine Sanctuary Fore Reef	24°31.96´N 81°24.22´W

TABLE 3. Mean values and ranges for nutrient concentrations (μM), temperature (°C) and salinity (o/oo) at canal, midpoint and septic locations in winter vs. summer. Groundwater represents the average of the the midpoint and septic values. Values represent means ± standard deviation.

LOCATION	N		NO3	NH4	SRP	N:P	TEMPERATURE	SALINITY
				WINTER				
CANAL	32	MEAN	1.61 ± 0.55	0.88 ± 0.29	0.15 ± 0.05	16.6	25.5 ± 3.1	37.1 ± 2.1
		RANGE	0.27------4.05	0.15------2.39	0.03-----0.35		19.0--30.1	33.0--42.0
MIDPOINT	28	MEAN	118.25 ± 179.89	256.94 ± 325.88	2.54 ± 2.83	147.7	25.2 ± 1.9	4.7 ± 3.4
		RANGE	0.03---545.45	3.61--2750.34	0.12---13.79		21.0--30.0	0.5--12.0
SEPTIC	32	MEAN	817.36 ±1052.80	784.89 ± 808.27	17.00 ± 26.85	94.3	26.0 ± 1.9	3.3 ± 3.9
		RANGE	6.69--2896.70	32.41--2417.79	0.14--107.39		21.0--29.3	0.0--19.0
GROUNDWATER		MEAN	467.81 ± 494.34	520.92 ± 373.32	9.77 ± 10.22	101.2	25.6 ± 0.6	4.0 ± 1.0
		RANGE	0.03--2896.70	3.61--2417.79	0.12--107.39		21.0--30.0	0.0--19.0
				SUMMER				
LOCATION	N		NO3	NH4	SRP	N:P	TEMPERATURE	SALINITY
CANAL	30	MEAN	3.22 ± 8.38	1.69 ± 1.48	0.43 ± 0.38	11.4	30.7 ± 1.3	40.9 ± 2.1
		RANGE	0.28-----49.02	0.33------6.92	0.12-----1.60		28.5--33.9	37.0--45.0
MIDPOINT	26	MEAN	30.76 ± 89.91	188.45 ± 306.32	1.63 ± 2.78	134.5	27.9 ± 1.9	15.2 ±12.4
		RANGE	0.04---409.02	0.77--1046.95	0.09---14.14		25.5--32.0	1.0--45.0
SEPTIC	30	MEAN	220.12 ± 482.13	502.97 ± 784.07	6.37 ± 16.28	113.5	28.1 ± 1.7	11.6 ±11.9
		RANGE	0.10--1969.71	3.60--2579.00	0.06---85.34		25.5--31.5	1.0--44.5
GROUNDWATER		MEAN	125.44 ± 133.89	345.71 ± 222.40	4.00 ± 3.35	117.8	28.0 ± 0.1	13.4 ± 2.5
		RANGE	0.04--1969.71	0.77--2579.00	0.06---85.34		25.5--32.0	1.0--45.0

TABLE 4. Statistical analysis (Kruskal-Wallis test) of summer vs. winter nitrate concentrations (μM) at residential sites and a control site at Key Deer National Wildlife Refuge. Values represent means ± standard deviation.

STATION	LOCATION	$\bar{X}$ SUMMER	N	$\bar{X}$ WINTER	N	P
PPH	CANAL	2.00 ± 1.41	10	1.71 ± 1.35	10	N.S.
	MIDPOINT	164.73 ± 212.56	6	258.46 ± 187.79	10	N.S.
	SEPTIC	1.17 ± 1.09	8	18.77 ± 10.04	10	<.001
EP	CANAL	1.32 ± 0.36	8	1.02 ± 0.32	10	N.S.
	MIDPOINT	0.57 ± 0.36	8	4.55 ± 2.62	10	<.001
	SEPTIC	196.49 ± 385.52	8	66.77 ± 71.77	10	N.S.
DA	CANAL	14.65 ± 23.20	8	1.31 ± 0.73	10	N.S.
	MIDPOINT	0.85 ± 0.83	6	277.25 ± 303.57	10	.001
	SEPTIC	393.91 ± 783.84	8	1989.61 ± 909.59	10	.004
DL	CANAL	2.21 ± 1.99	8	0.47 ± 0.55	10	.047
	MIDPOINT	2.03 ± 3.13	8	9.02 ± 11.92	10	N.S.
	SEPTIC	2.54 ± 2.42	8	350.28 ± 527.79	10	<.001
WP	CANAL	0.98 ± 0.49	8	2.18 ± 1.63	8	N.S.
	MIDPOINT	2.93 ± 2.10	8	8.58 ± 4.89	8	.019
	SEPTIC	340.60 ± 244.70	8	197.07 ± 249.98	8	N.S.
YT	CANAL	4.32 ± 4.27	8	2.43 ± 1.04	8	N.S.
	SEPTIC	496.33 ± 982.26	8	2742.03 ± 150.83	8	.001
TH	CANAL	1.05 ± 0.63	8	1.65 ± 1.00	8	N.S.
	MIDPOINT	53.92 ± 105.97	8	6.93 ± 10.88	8	N.S.
	SEPTIC	194.35 ± 385.22	8	506.59 ± 842.36	8	.034
KDR	CONTROL	0.20 ± 0.23	8	0.76 ± 1.20	12	N.S.

N.S. = P>0.05

TABLE 5. Statistical analysis (Kruskal-Wallis test) of summer vs. winter ammonium concentrations (μM) at residential sites and a control site at Key Deer National Wildlife Refuge. Values represent means ± 1 standard deviation.

STATION	LOCATION	$\bar{X}$ SUMMER	N	$\bar{X}$ WINTER	N	P
PPH	CANAL	1.88 ± 1.33	10	0.62 ± 0.21	10	.003
	MIDPOINT	11.18 ± 9.95	6	16.38 ± 12.41	10	N.S.
	SEPTIC	37.73 ± 3.46	8	83.89 ± 59.62	10	.001
EP	CANAL	1.74 ± 0.45	8	0.84 ± 0.13	10	<.001
	MIDPOINT	16.49 ± 11.13	8	23.63 ± 9.99	10	N.S.
	SEPTIC	2311.19 ± 252.22	8	2146.90 ± 473.46	10	N.S.
DA	CANAL	2.69 ± 2.95	8	0.81 ± 0.51	10	.035
	MIDPOINT	200.71 ± 132.34	6	62.86 ± 43.89	10	.016
	SEPTIC	743.08 ±1175.76	8	1415.57 ± 778.03	10	N.S.
DL	CANAL	0.83 ± 0.83	8	0.50 ± 0.23	10	N.S.
	MIDPOINT	19.21 ± 13.22	8	27.71 ± 10.29	10	N.S.
	SEPTIC	28.99 ± 7.09	8	201.57 ± 224.91	9	.007
WP	CANAL	2.24 ± 1.72	8	1.03 ± 1.03	8	N.S.
	MIDPOINT	188.10 ± 59.39	8	137.80 ± 51.25	8	.018
	SEPTIC	507.51 ± 191.99	8	259.79 ± 176.84	8	N.S.
YT	CANAL	1.35 ± 1.32	8	0.96 ± 0.75	8	N.S.
	SEPTIC	156.0 ± 274.36	8	254.50 ± 169.63	8	N.S.
TH	CANAL	1.55 ± 0.75	8	1.40 ± 0.67	8	N.S.
	MIDPOINT	939.86 ± 109.74	8	146.12 ± 9.00	8	N.S.
	SEPTIC	603.54 ± 198.55	8	1588.40 ± 400.84	8	.001
KDR		1.40 ± 0.48	8	1.91 ± 1.39	12	N.S.

N.S. = P>0.05

TABLE 6. Statistical analysis (Kruskal-Wallis test) of summer vs. winter soluble reactive phosphate (µM) concentrations at residential sites and a control site at the Key Deer National Wildlife Refuge. Values represent means ± 1 standard deviation.

STATION	LOCATION	$\overline{X}$ SUMMER	N	$\overline{X}$ WINTER	N	P
PPH	CANAL	0.32 ± 0.21	8	0.08 ± 0.02	10	<.001
	MIDPOINT	0.43 ± 0.17	8	0.97 ± 0.78	10	N.S.
	SEPTIC	0.15 ± 0.07	8	0.92 ± 0.81	10	<.001
EP	CANAL	0.30 ± 0.18	8	0.13 ± 0.03	10	.008
	MIDPOINT	0.23 ± 0.17	8	0.86 ± 0.97	10	.016
	SEPTIC	18.16 ± 7.62	8	65.82 ± 38.07	10	.029
DA	CANAL	0.94 ± 0.66	8	0.19 ± 0.09	10	.008
	MIDPOINT	2.14 ± 0.65	8	4.92 ± 3.05	10	.031
	SEPTIC	2.26 ± 0.86	8	5.46 ± 2.32	10	.001
DL	CANAL	0.25 ± 0.15	8	0.15 ± 0.06	10	N.S.
	MIDPOINT	6.05 ± 5.40	8	7.15 ± 4.08	10	.029
	SEPTIC	0.84 ± 0.72	8	0.77 ± 0.37	10	.001
WP	CANAL	0.68 ± 0.64	8	0.12 ± 0.02	8	.002
	MIDPOINT	0.70 ± 0.18	8	0.50 ± 0.18	8	N.S.
	SEPTIC	0.23 ± 0.14	8	0.51 ± 0.21	8	.006
YT	CANAL	0.35 ± 0.17	8	0.15 ± 0.07	8	.011
	SEPTIC	24.73 ± 40.54	8	44.53 ± 32.94	8	N.S.
TH	CANAL	0.37 ± 0.11	8	0.22 ± 0.06	8	.015
	MIDPOINT	0.44 ± 0.18	8	0.76 ± 0.43	8	N.S.
	SEPTIC	0.67 ± 0.88	8	1.08 ± 1.02	8	N.S.
KDR	CONTROL	0.14 ±0.11	8	0.11 ± 0.02	12	N.S.

N.S.= P>0.05

TABLE 7. Statistical analysis (Kruskal-Wallis test) to determine differences in nutrient concentrations at residential stations and the control station at Key Deer National Wildlife Refuge. Values represent the probability that no difference exists between residential sites and the control station; N.S.= not significant (P >.05).

LOWER KEYS

WINTER				SUMMER			
LOCATION	NO3	NH4	SRP	LOCATION	NO3	NH4	SRP
PPHM	<.001	.001	<.001	PPHM	.002	.117	.002
PPHS	<.001	<.001	<.001	PPHS	.012	.001	N.S.
EPM	<.001	<.001	<.001	EPM	N.S.	.056	N.S.
EPS	<.001	<.001	<.001	EPS	N.S.	.001	.001
DAM	<.001	<.001	<.001	DAM	.037	.002	.001
DAS	<.001	<.001	<.001	DAS	.001	.001	.001
WPM	.001	<.001	<.001	WPM	.001	.001	.001
WPS	<.001	<.001	<.001	WPS	.001	.001	N.S.

UPPER KEYS

WINTER				SUMMER			
LOCATION	NO3	NH4	SRP	LOCATION	NO3	NH4	SRP
DLM	.045	<.001	<.001	DLM	N.S.	.001	.001
DLS	<.001	<.001	.008	DLS	.012	.001	N.S.
THM	.008	<.001	<.001	THM	.055	.001	.004
THS	<.001	<.001	<.001	THS	.003	.001	N.S.
YTS	<.001	<.001	<.001	YTS	.003	.001	.001
OSM	---	---	---	OSM	.002	.006	.002
OSS	---	---	---	OSS	.019	.002	.002

TABLE 8. Mean values for nutrients (μM) and salinity (parts per thousand) for Halcyon Trailer Park and Key Deer National Wildlife Refuge. Values represent $\pm$ 1 standard deviation.

LOCATION	NO_3	NH_4	SRP	SALINITY
KDNWR-30´	0.07 ± 0.02	5.67 ± 7.00	0.12 ± 0.08	2.0 ± 0.0
KDNWR-60´	0.33 ± 0.21	1.03 ± 0.46	0.13 ± 0.12	0.3 ± 0.6
HTP-MF	2691.29 ± 518.15	203.29 ± 342.33	117.06 ± 6.46	2.9 ± 2.7
HTP-60´	0.13 ± 0.04	17.96 ± 4.37	0.74 ± 0.38	41.8 ± 2.9
HTP-30´	0.29 ± 0.24	19.05 ± 7.34	0.93 ± 0.50	39.5 ± 1.1
HTP-15´	2.63 ± 4.11	20.29 ± 8.49	0.34 ± 0.18	22.2 ± 7.1
HTP-Open Water	0.44 ± 0.19	0.91 ± 0.94	0.35 ± 0.17	42.6 ± 3.0

TABLE 9. Rate and direction of groundwater flow during a flooding and ebbing tide at Port Pine Heights, Big Pine Key, FL. * Denotes occurrence of a heavy rain event.

LOCATION	DATE	TIME	TIDE	RATE(ft/d)	DIRECTION
PPH	7-24-87	1215	Flooding	2.58	199°
		1345	High	0.00	----
		1515	Ebbing	2.21	193°
		1800	Ebbing	5.00	188°
		1930	Ebbing	2.64	163°
		2130	Ebbing	1.52	176°
		2300	Low	2.08	181°
PPH -- Average			Ebbing	2.29	183°
PPH	10-02-87	1830	Low	2.83	190°
		2130	Flooding	12.10*	222°
		2300	Flooding	9.68*	160°
	10-03-87	0320	Flooding	4.19*	172°
		1130	High	3.32	187°
		1500	Ebbing	3.73	174°
		2230	Low	2.83	190°
PPH -- Average			Flooding	6.40	185°

* Heavy rain event

TABLE 10. Rate and direction of groundwater flow at Halcyon Trailer Park (HTP) and the Key Deer National Wildlife Refuge (KDNWR) at different depths and tides.

LOCATION	DATE	TIME	TIDE	RATE(ft/d)	DIRECTION
HTP 15´	8-09-87	1500	High	2.17	305°
HTP 15´	10-20-87	1830	Low	3.32	277°
HTP 60´	8-09-87	1330	High	2.17	197°
HTP 30´	10-20-87	1730	Low	1.21	188°
KDNWR 15´	8-08-87	1345	High	0.00	----
KDNWR 15´	10-15-87	1710	Low	0.75	71°
KDNWR 30´	8-08-87	1515	High	3.38	104°
KDNWR 30´	10-15-87	1750	Low	4.10	87°

TABLE 11. Mean values and ranges of nutrient concentrations (µM) and chlorophyll-a (µg/1) along an onshore-offshore transect from inshore canal waters on Big Pine Key (PPH) to offshore waters at Looe Key National Marine Sanctuary (LK). Values represent means ± 1 standard deviation.

STATION		NO3	NH4	SRP	EN:P	Chl-a
1---PPH-BEL	MEAN	1.60 ± 0.92	0.57 ± 0.23	0.09 ± 0.07	24.1	0.34 ± 0.22
	RANGE	0.39---3.02	0.22---0.94	0.03---0.29		0.09---0.78
2---PPH-MAIN	MEAN	1.67 ± 0.57	0.49 ± 0.18	0.07 ± 0.05	30.8	0.19 ± 0.09
	RANGE	0.38---2.36	0.18---0.79	0.03---0.22		0.07---0.42
3---PINE CHANNEL	MEAN	0.84 ± 0.32	0.32 ± 0.12	0.05 ± 0.02	23.2	0.14 ± 0.06
	RANGE	0.26---1.29	0.12---0.48	0.03---0.10		0.06---0.21
4---LITTLE MUNSON IS.	MEAN	0.78 ± 0.42	0.27 ± 0.11	0.05 ± 0.02	21.0	0.22 ± 0.11
	RANGE	0.27---1.75	0.09---0.49	0.03---0.08		0.08---0.50
5---HAWKS CHANNEL	MEAN	0.40 ± 0.34	0.16 ± 0.07	0.05 ± 0.03	11.2	0.24 ± 0.13
	RANGE	0.13---1.05	0.05---0.31	0.03---0.11		0.09---0.50
6---LK-BACK REEF	MEAN	0.40 ± 0.32	0.21 ± 0.16	0.05 ± 0.02	12.2	0.18 ± 0.09
	RANGE	0.14---0.94	0.02---0.06	0.03---0.10		0.10---0.43
7S--LK-FORE REEF SURFACE	MEAN	0.38 ± 0.33	0.23 ± 0.14	0.04 ± 0.02	15.3	0.13 ± 0.07
	RANGE	0.08---0.96	0.02---0.53	0.03---0.08		0.05---0.32
7B--LK-FORE REEF BOTTOM	MEAN	0.52 ± 0.38	0.22 ± 0.09	0.06 ± 0.04	12.3	0.19 ± 0.10
	RANGE	0.14---1.35	0.02---0.33	0.03---0.16		0.07---0.37

TABLE 12. Correlation matrices of nutrient concentrations and chlorophyll-a data along and onshore-offshore transect from inshore canal waters on Big Pine Key to offshore waters of Looe Key National Marine Sanctuary (LK). Data were collected at samplings from 10/17/86 to 6/19/87. Values represent correlation coefficients; *r >0.70 is considered significant.

10/17/86 LK #1	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.82 *	.67	.52
AMMONIA		.66	.82 *
PHOSPHATE			.80 *

11/15/86 LK #2	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.68	.52	.86 *
AMMONIA		.47	.49
PHOSPHATE			.76 *

11/23/86 LK #3	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.96 *	.35	.78 *
AMMONIA		.41	.68
PHOSPHATE			.13

12/06/86 LK #4	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.89 *	.66	.11
AMMONIA		.82 *	.05
PHOSPHATE			.39

12/21/86 LK #5	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.96 *	.94 *	.81 *
AMMONIA		.93 *	.78 *
PHOSPHATE			.88 *

1/08/87 LK #6	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.91 *	.95 *	.27
AMMONIA		.79 *	.40
PHOSPHATE			.24

TABLE 12. CONTINUED

1/28/87 LK #7	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.91 *	.72 *	.59
AMMONIA		.81 *	.47
PHOSPHATE			.70 *

2/18/87 LK #8	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.84 *	.27	.34
AMMONIA		.37	.43
PHOSPHATE			.12

3/20/87 LK #9	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.81 *	.29	.32
AMMONIA		.21	.39
PHOSPHATE			.31

4/09/87 LK #10	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.85 *	.18	.04
AMMONIA		.11	.30
PHOSPHATE			.49

4/26/87 LK #11	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.68	.02	.31
AMMONIA		.45	.36
PHOSPHATE			.86 *

6/19/87 LK #12	AMMONIA	PHOSPHATE	CHLOROPHYLL
NITRATE	.63	.55	.37
AMMONIA		.93	.65
PHOSPHATE			.79 *

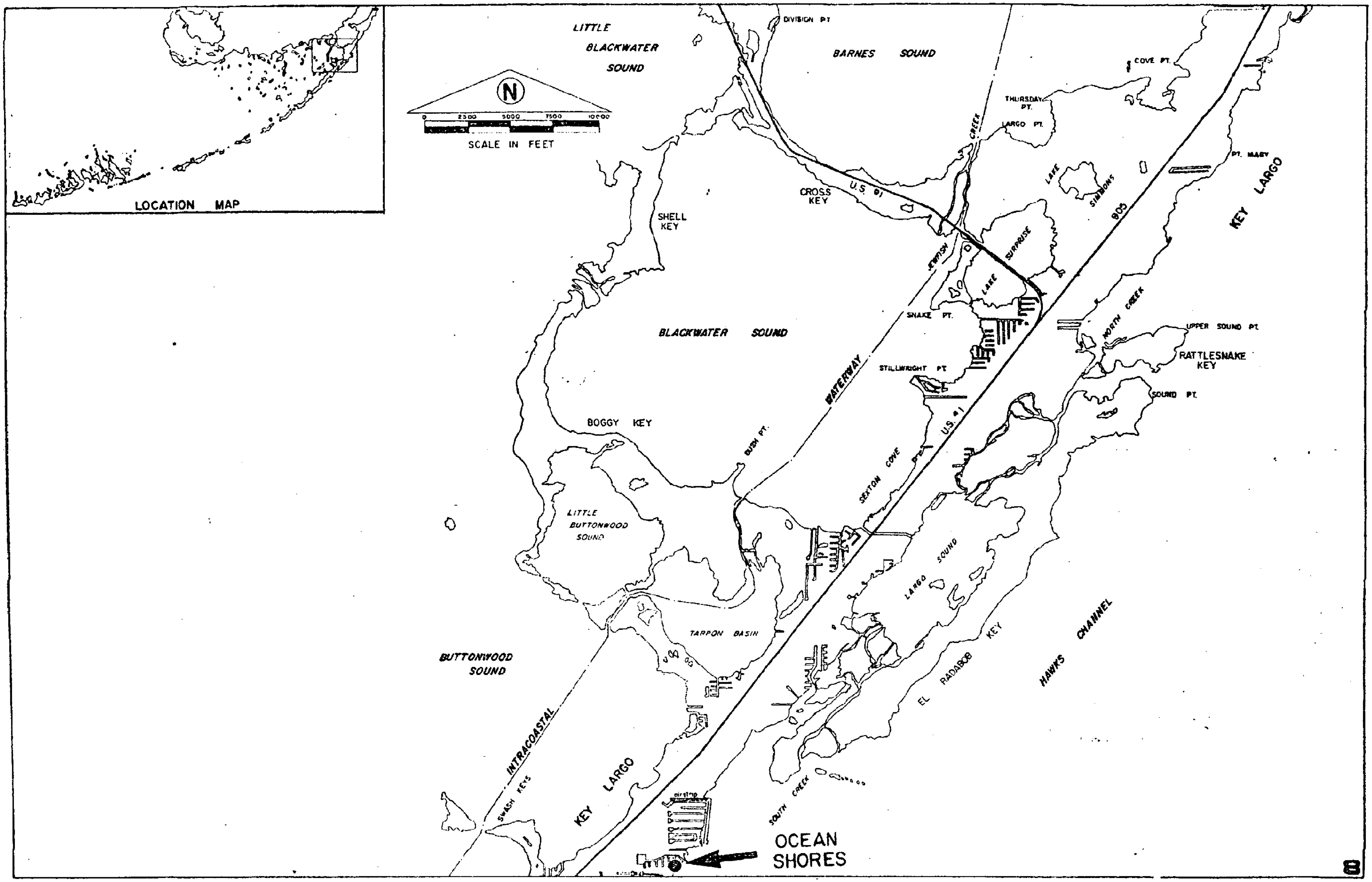


Figure 1. Location of groundwater monitor stations on Key Largo.

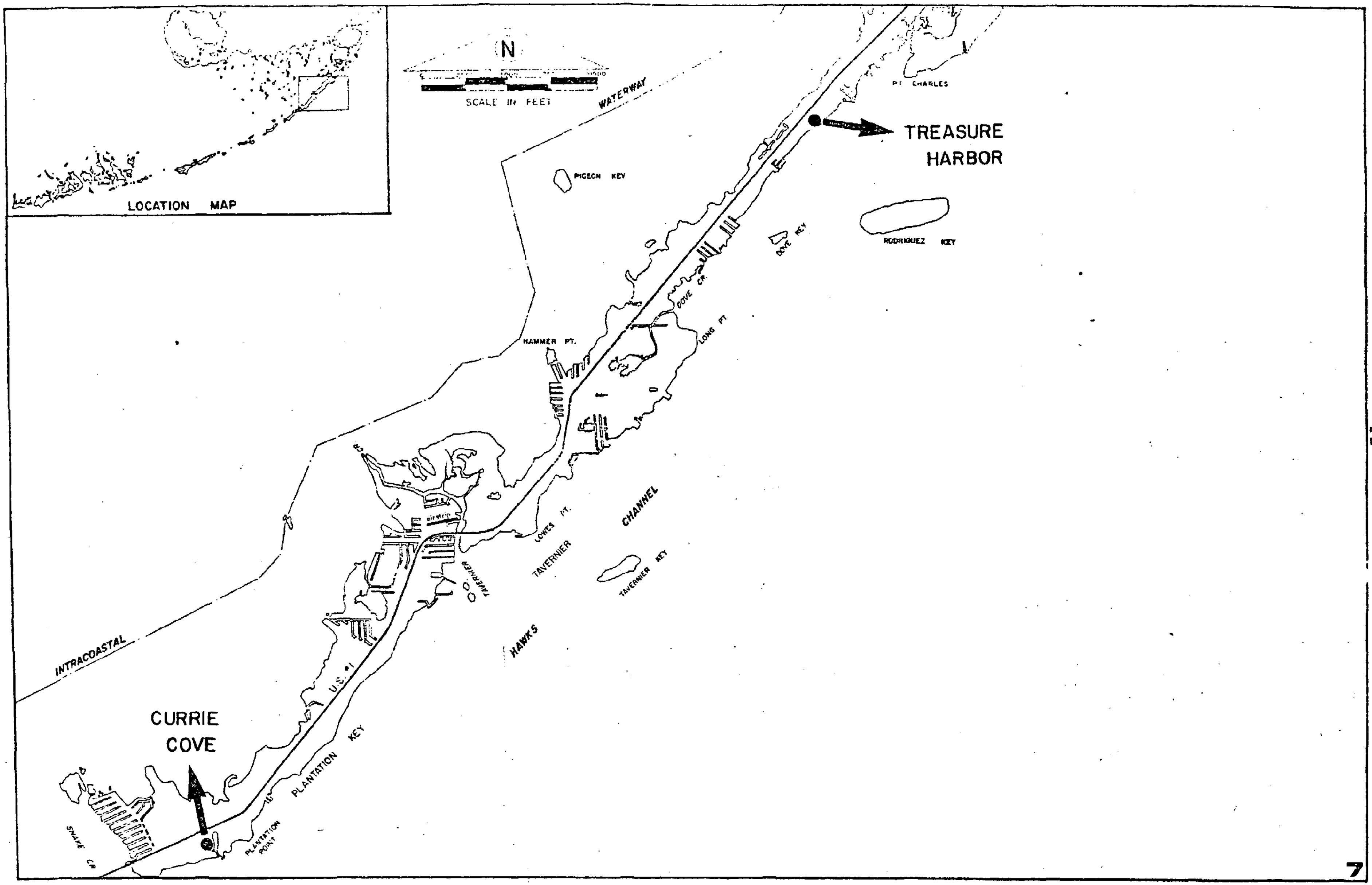


Figure 2. Location of groundwater monitor stations on Plantation Key.

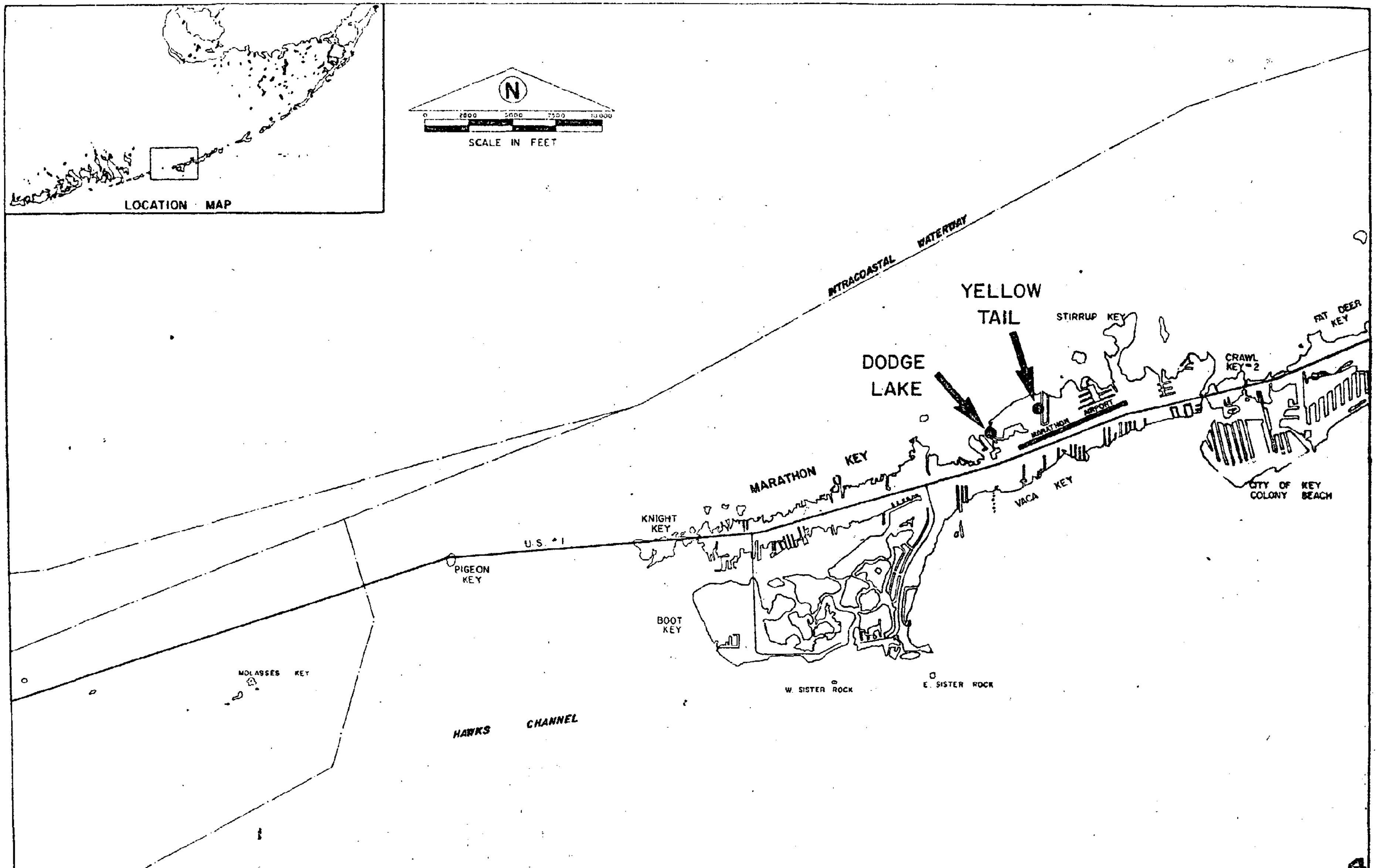


Figure 3. Location of groundwater monitor stations on Marathon.

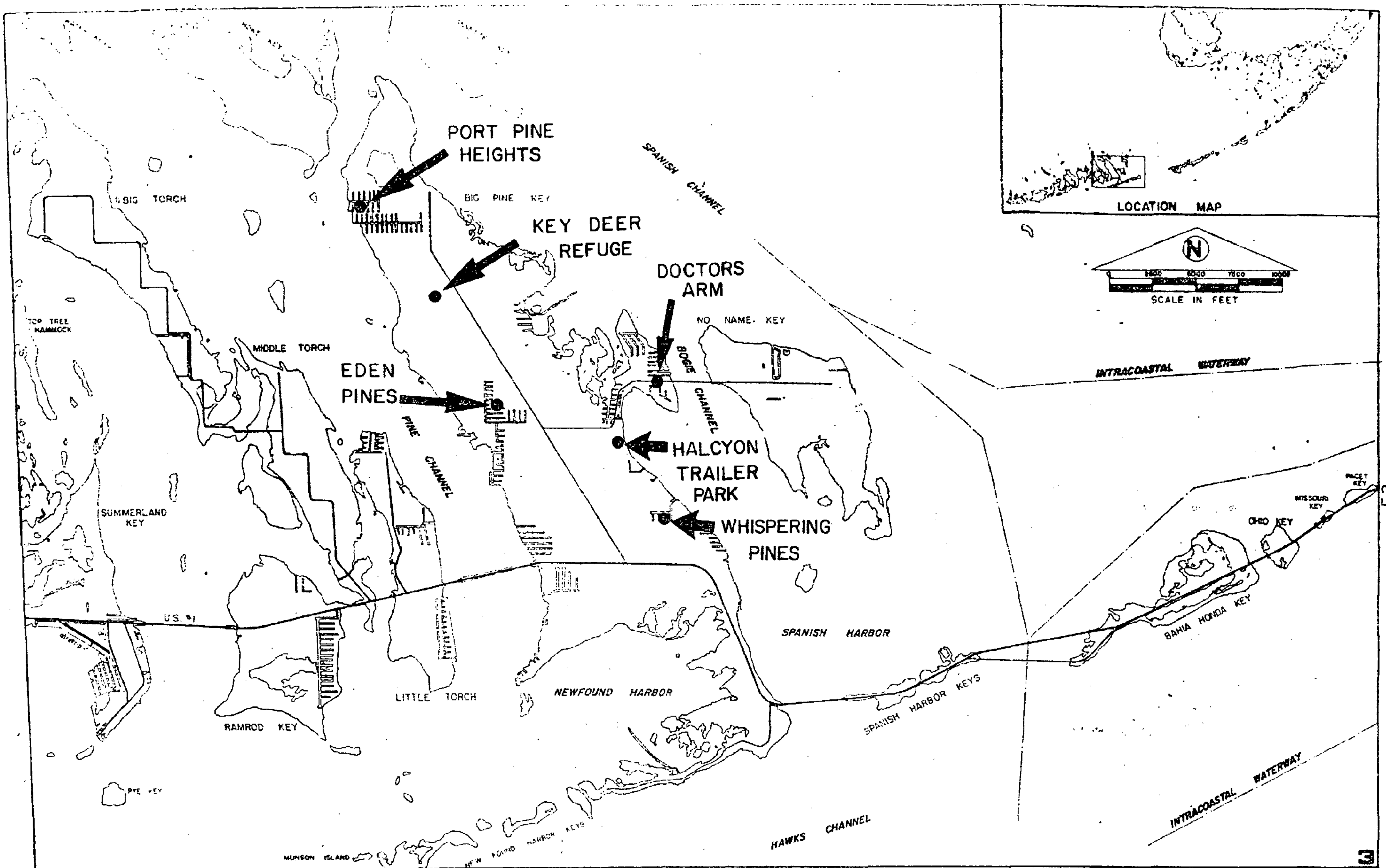
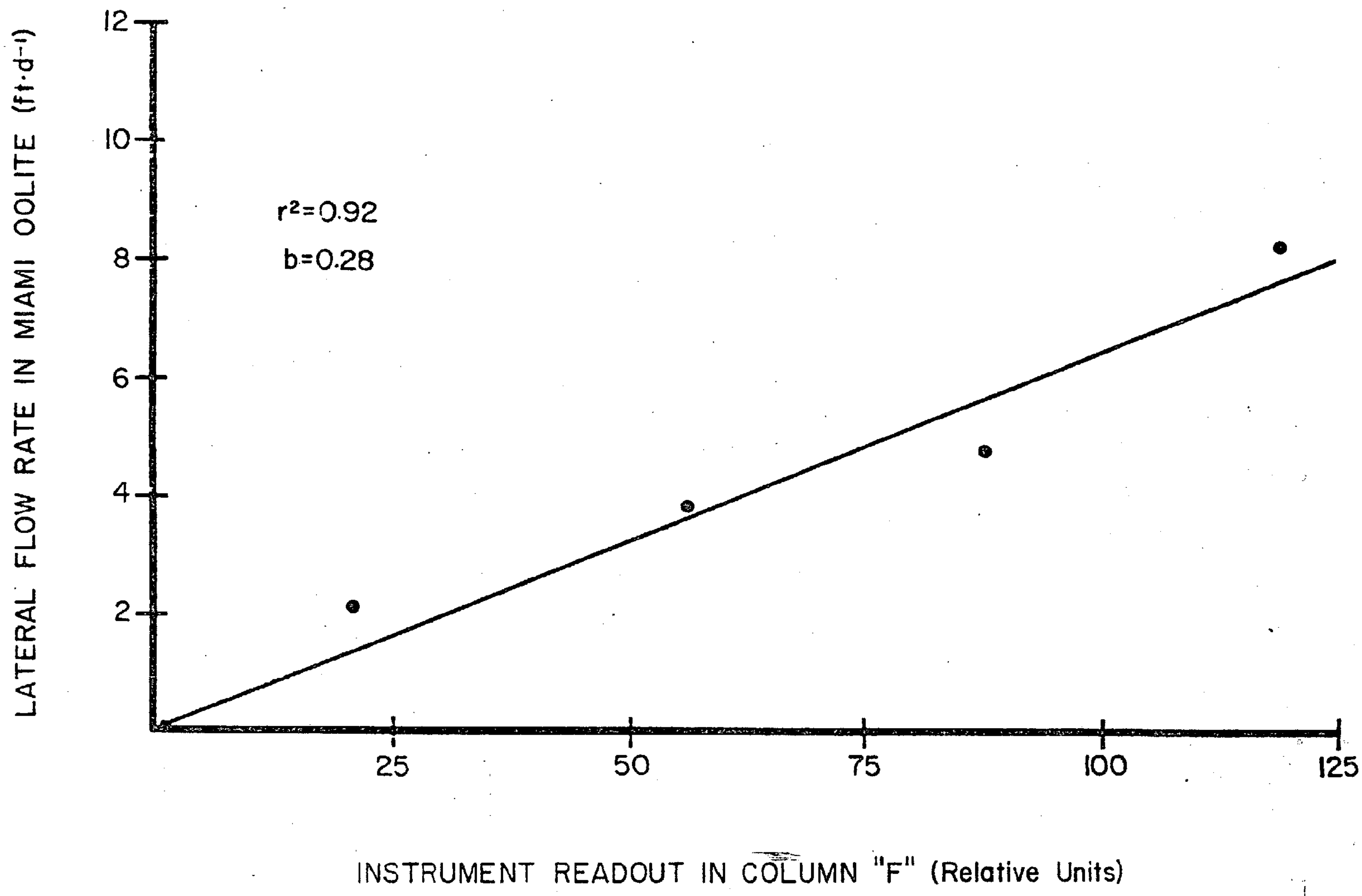


Figure 4. Location of groundwater monitor stations on Big Pine Key.

Figure 5. Calibration Curve for GeoFlow groundwater flow meter.



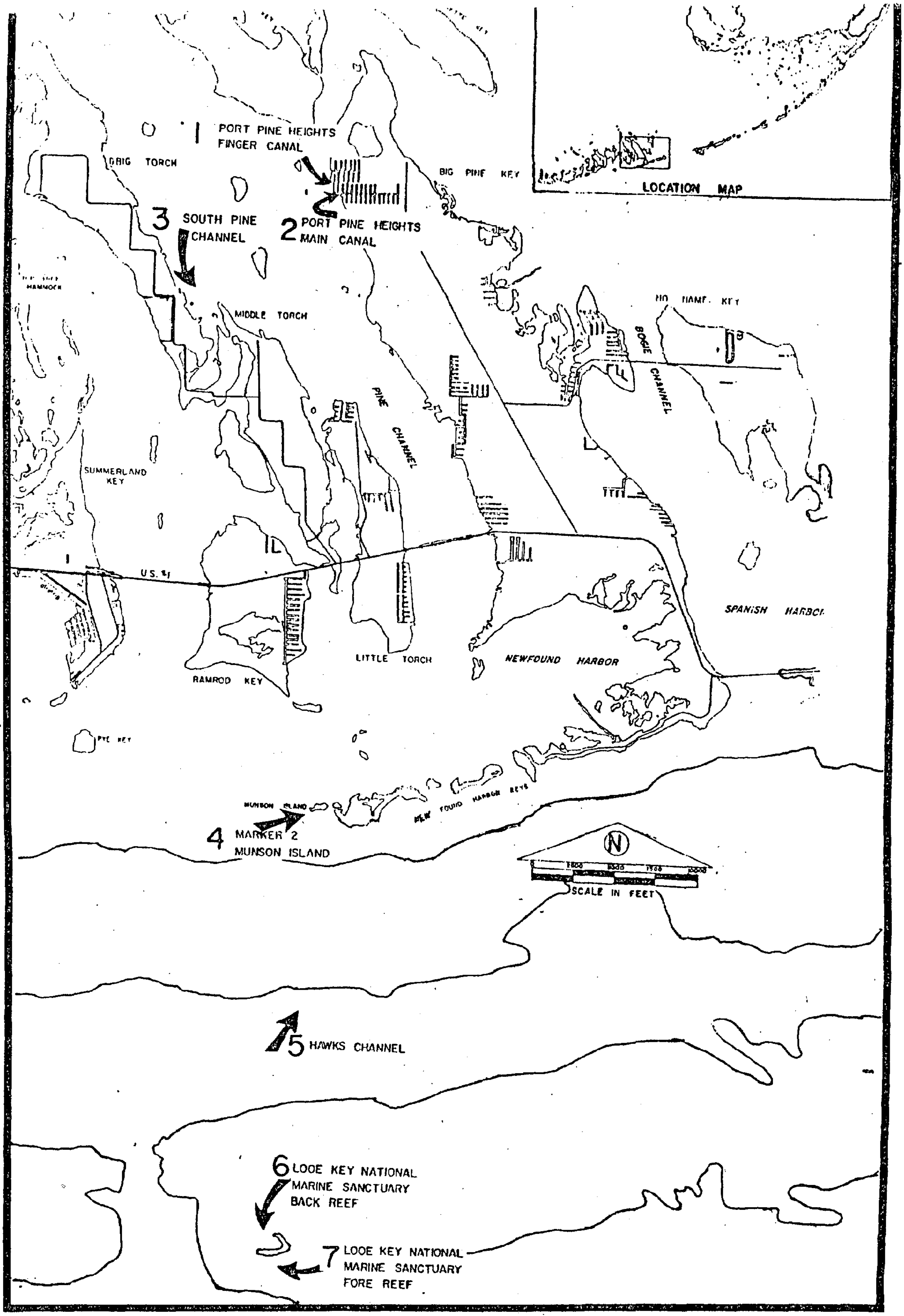


Figure 6. Location of hydrographic stations in nearshore waters of Big Pine Key.

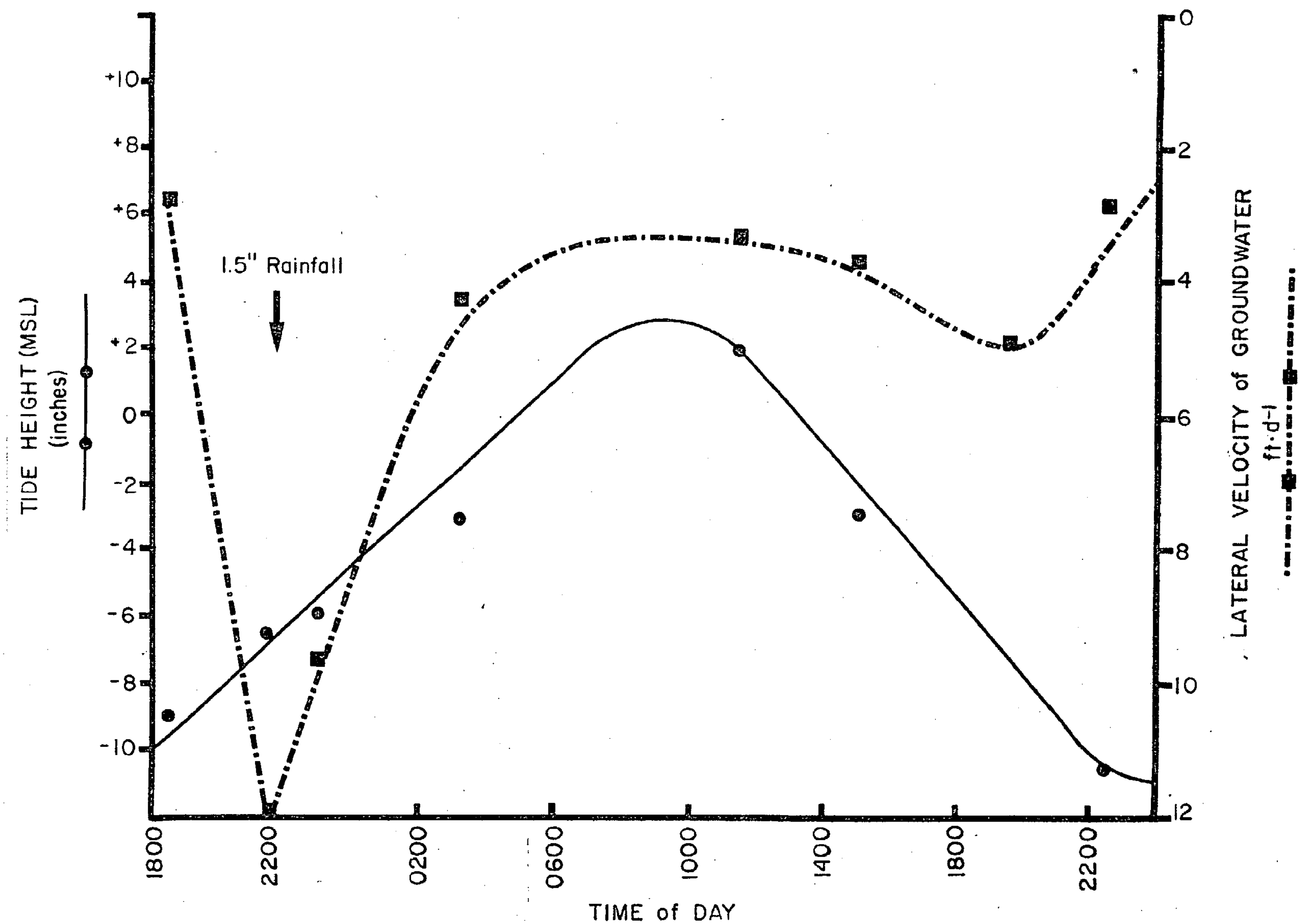


Figure 7. Groundwater flow rate in Port Pine Heights, Big Pine Key; ebbing tide.

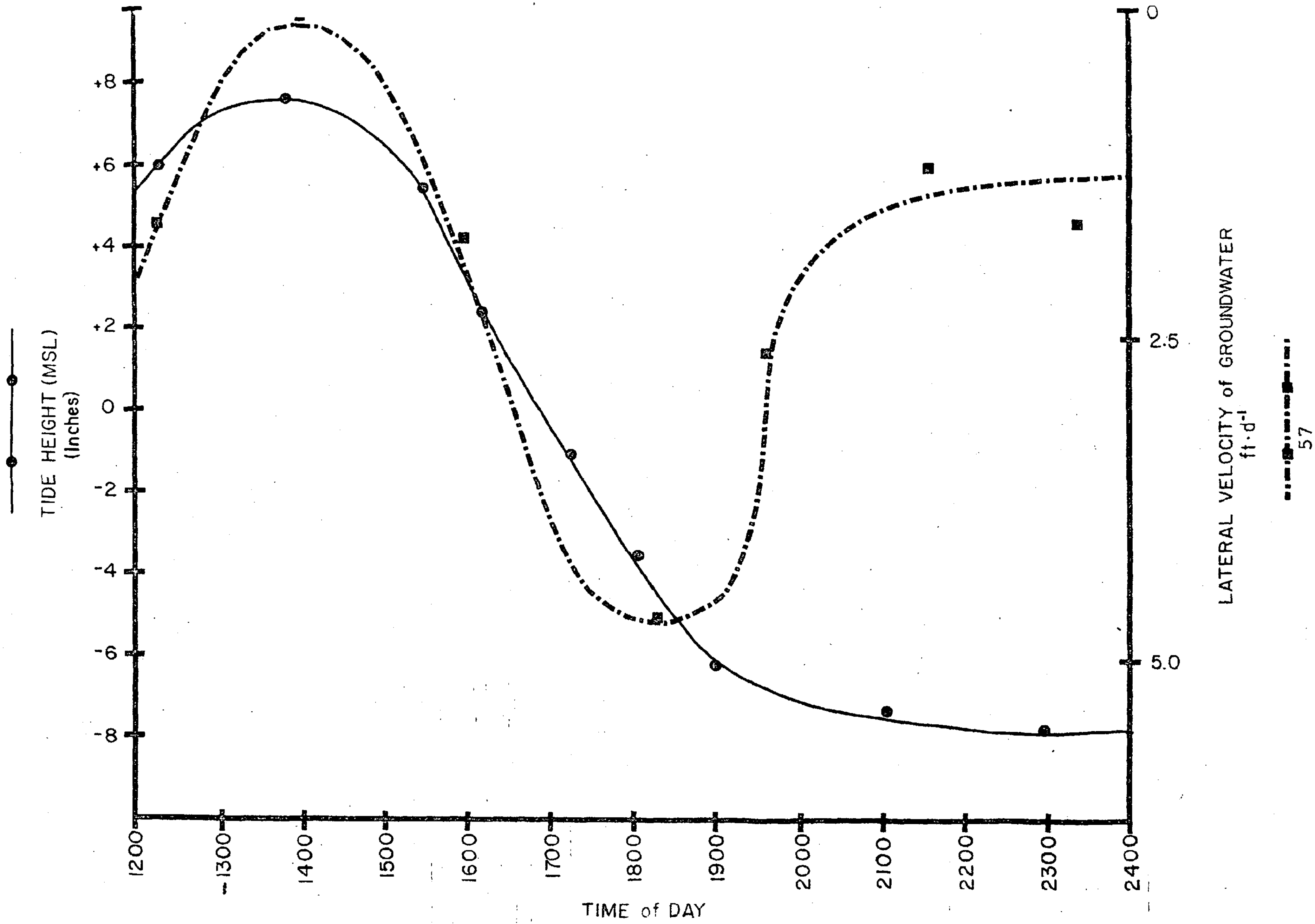


Figure 8. Groundwater flow rate in Port Pine Heights, Big Pine Key; flooding tide.

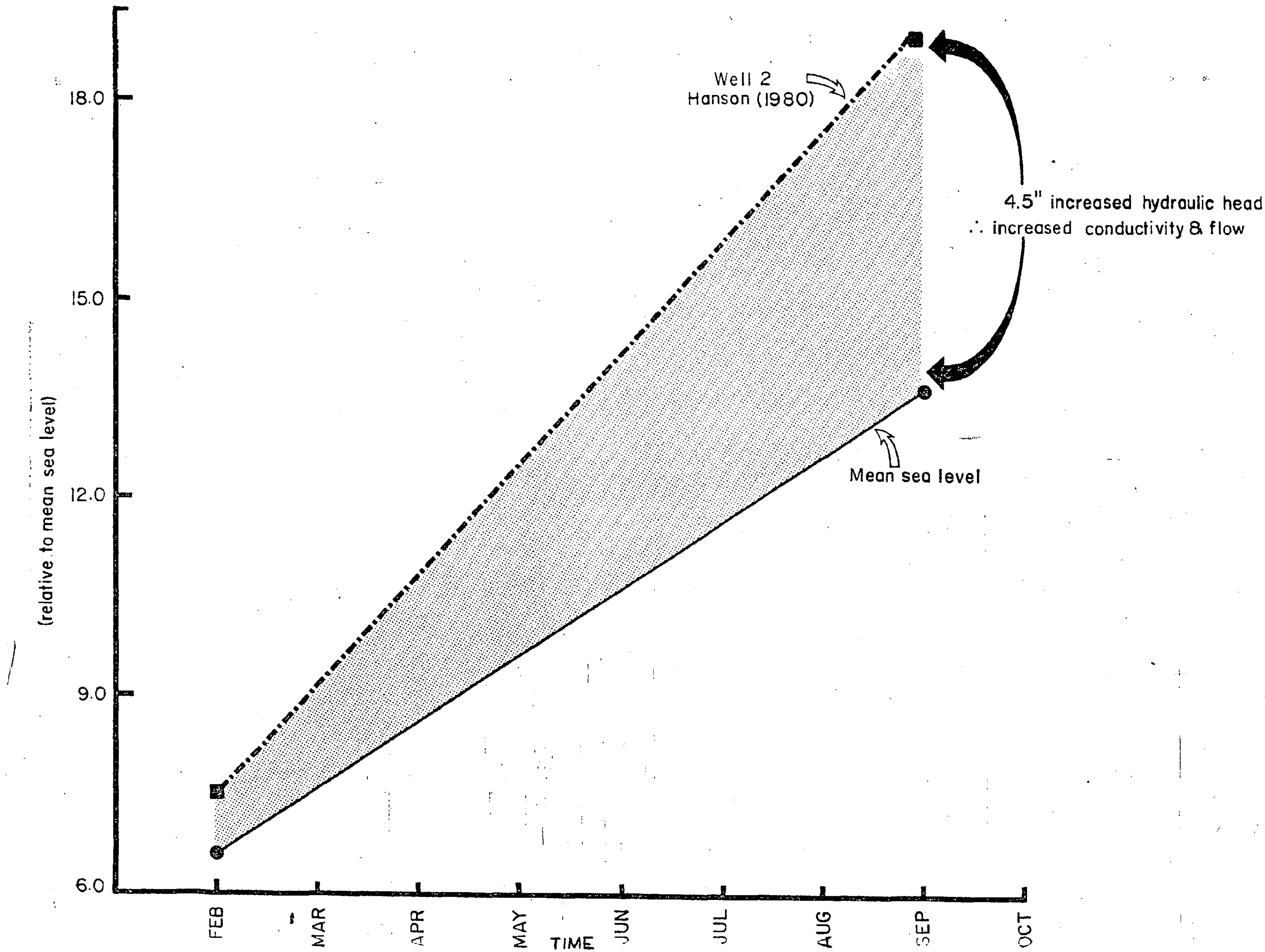


Figure 9. Seasonal trends in hydraulic head based on monthly average groundwater table height and mean sea level